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Ignition of $\text{SiH}_4\text{-H}_2\text{-O}_2\text{-N}_2$ Behind Reflected Shock Waves

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Ignition of $\text{SiH}_4\text{-H}_2\text{-O}_2\text{-N}_2$ Behind Reflected Shock Waves

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National Aeronautics
and Space Administration

Scientific and Technical
Information Branch

INTRODUCTION

One of the challenges in the development of a hydrogen-fueled, combustion ramjet engine is to assure that combustion is maintained over the entire pressure-temperature regime encountered. A major problem has been the uncertainty in ignition delay times for the candidate fuel. To cope with this problem, the use of combustion initiators is being seriously considered. The addition of a combustion initiator would ensure combustion during critical regions of pressure and temperature, which are dependent on vehicular speed, altitude, and other flight characteristics. One of the most promising combustion initiators being considered presently is silane, SiH_4 .

Experiments in the Langley Research Center Hypersonic Propulsion Test Cells and at contractor facilities have demonstrated that the addition of silane to hydrogen fuel enhances combustion and also helps sustain stable combustion (ref. 1). A chemical kinetic mechanism for the silane-hydrogen system was suggested by Beach et al. (ref. 2). Calculations with this mechanism also showed that significant reduction in ignition delay times is possible when silane is added to hydrogen-air mixtures.

The objective of the study reported here was to quantitatively characterize the ignition characteristics of silane-hydrogen mixtures and to use the results to test the mechanism proposed by Beach et al. (ref. 2). The experimental study was carried out in a chemical kinetic shock tube. Ignition delay times were measured behind reflected shock waves for two silane-hydrogen-oxygen-nitrogen mixtures at test conditions which duplicate pressures and temperatures which are likely to occur within a supersonic ramjet combustor. The measured ignition delay times were compared with the ignition delay times predicted by the silane-hydrogen reaction model. The theoretical comparisons were made with a computer program which simulates the chemical kinetics behind reflected shock waves (ref. 3). The thermochemical data used in making the theoretical comparisons were taken from the literature, primarily JANAF (ref. 4). For some fragmentary compounds deemed necessary to describe the silane combustion process, thermochemical properties were estimated.

EXPERIMENTAL APPARATUS AND MEASUREMENTS

All the experimental measurements were made behind reflected shock waves in a stainless steel tube with an inside diameter of 8.9 cm. The test section was 671 cm long. The present arrangement differed from that shown in references 5 and 6 in that the dump tank was removed and replaced with a flat stainless steel plate. Fast-response, transient pressure transducers were spaced every 30.48 cm along the last 122 cm of the test section. The test section and instrumentation locations are shown in figure 1. The flat plate located at the end wall of the shock tube was machined to accept a transient pressure transducer at the axial centerline of the shock tube. The pressure transducer placed here actually protruded 3 mm into the approaching shock wave and incoming flow. Ignition measurements were made at this location.

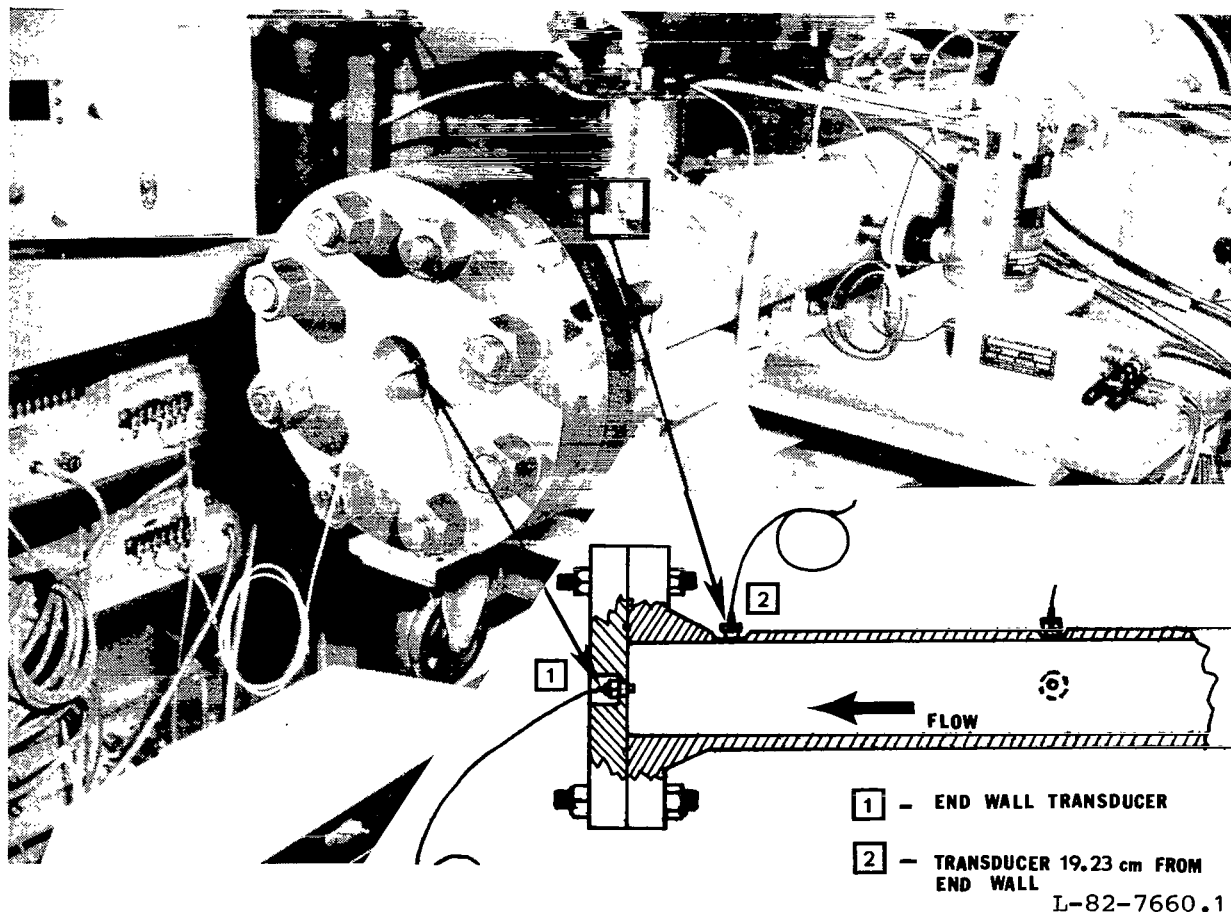


Figure 1.- Photograph and schematic representation of shock tube test section for reflected shock waves.

The information from the passage of the incident shock wave sensed by each transducer was recorded by a digital oscilloscope. The incident shock velocity, which was used to calculate the conditions behind the reflected shock wave, was obtained by using the time differential between the recorded signals of the transducers located 19.23 cm and 3 mm from the end wall. These two transducers were separated by 18.93 cm. The measured velocities resulted in calculated, incident-shock-wave Mach numbers ranging from about 2 to 3. The time constant for the pressure measurements was $4 \mu\text{s} \pm 0.5 \mu\text{s}$ for the entire series of tests.

The shock tube was filled to a pressure of 40 mm of mercury with test gas for all the experiments. After approximately seven tests, the shock tube was disassembled and cleaned. This need for cleaning resulted partly from the debris of the diaphragms but mostly from the oxides of silicon powder formed from silane combustion. Once deposited on the shock tube walls, the powdered silicon oxides remained in place.

Two gas mixtures with silane-oxygen equivalence ratios of 1.0 and 0.5 were used for the tests. The compositions of the test gas mixtures for silane-oxygen equivalence ratios of 1.0 and 0.5 are given in tables I(a) and I(b), respectively.

These mixtures were obtained by diluting with nitrogen a commercially supplied mixture of 20 mole-percent silane and 80 mole-percent hydrogen. This $\text{SiH}_4\text{-H}_2\text{-N}_2$ mixture was mixed with air in the shock tube to obtain the desired silane-oxygen

stoichiometry in the test gas. This was implemented to prevent oxidation of the silane, which was observed to occur when premixing H_2 - SiH_4 - O_2 - N_2 at pressures above 1 atm in the mixing vessel. When mixing was effected in the shock tube at pressures of 40 mm of mercury, no evidence of silane oxidation was noted (as would have been observed by the visible formation of a white silicon oxide deposit).

EXPERIMENTAL RESULTS AND DATA ANALYSIS

An example of the pressure histories behind both the incident shock wave and the reflected shock wave is shown in figure 2. Figure 2(a) shows the pressure history measured by the transducer 19.23 cm from the end wall of the shock tube. As can be seen, the pressure quickly increases from the vacuum value to the pressure behind the incident shock wave (0.32 atm). Approximately 700 μs later, the shock wave, after reflection off the end wall, again passes the transducer and quickly raises the pressure level to approximately 1.25 atm. In figure 2(b), the pressure history 3 mm from

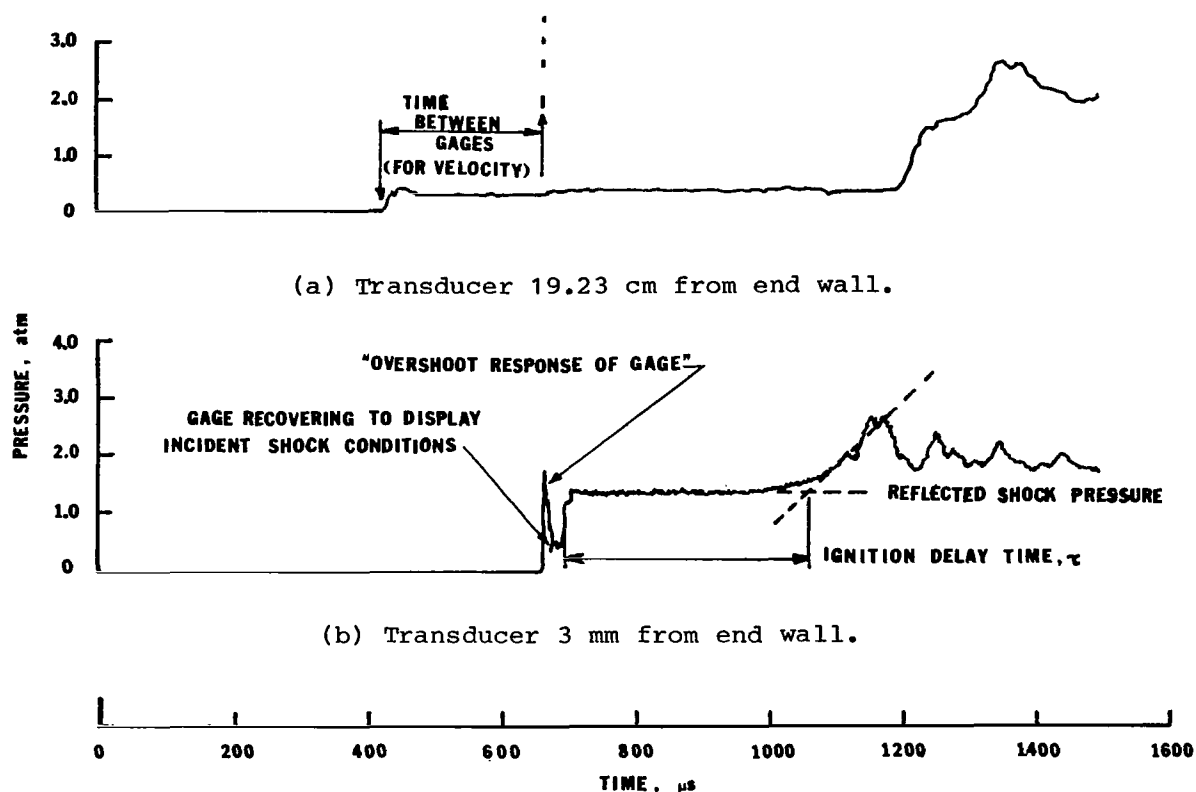


Figure 2.- Typical pressure histories for mixture II test gas after shock wave passage. Pressure = 1.35 atm.

the end wall may be observed. The first increase in pressure occurs when the shock wave initially encounters the transducer. For the end-on placed transducer, in all cases, the record was found to exhibit "ringing" or "overshoot." However, after passage of the shock wave, the pressure drops back toward the normal pressure level (≈ 0.3 atm) behind an incident shock wave, as is labeled in the figure. After the

shock wave is reflected from the end wall of the shock tube (and travels the 3 mm), the pressure increases to the value of 1.25 atm behind a reflected shock wave. Approximately 200 μ s later (for the mixture illustrated), the mixture ignites. The ignition delay or induction time is measured from the point at which the pressure history exhibits its maximum slope after reflection of the shock wave, to the maximum slope reached after leveling off behind the reflected shock wave.

The incident shock velocity needed in the calculation of the reflected shock wave conditions was obtained from the time difference between the transducers placed 19.23 cm from the end wall and 3 mm from the end wall, as shown in figure 2.

The measured ignition delay times τ for the silane-hydrogen-air mixtures are shown in tables II(a) and II(b) along with the associated initial (unreacted) temperatures behind the reflected shock wave. The mixtures containing silane required from 24 to 752 μ s to ignite after passage of the reflected shock wave. The initial reflected shock temperatures were calculated from the incident shock speed with the assumption of no reaction behind the incident wave. These values ranged from approximately 800 K to 1050 K. The observed pressures just behind the reflected shocks were within 3 to 5 percent of those calculated, and the estimated uncertainty in the initial reflected shock temperature is no more than ± 10 K. The analytical model used to calculate the conditions behind the reflected shock wave is described in reference 3. The variation of the experimentally measured ignition delay times over a range of temperatures is shown in figure 3 for a silane-oxygen equivalence ratio

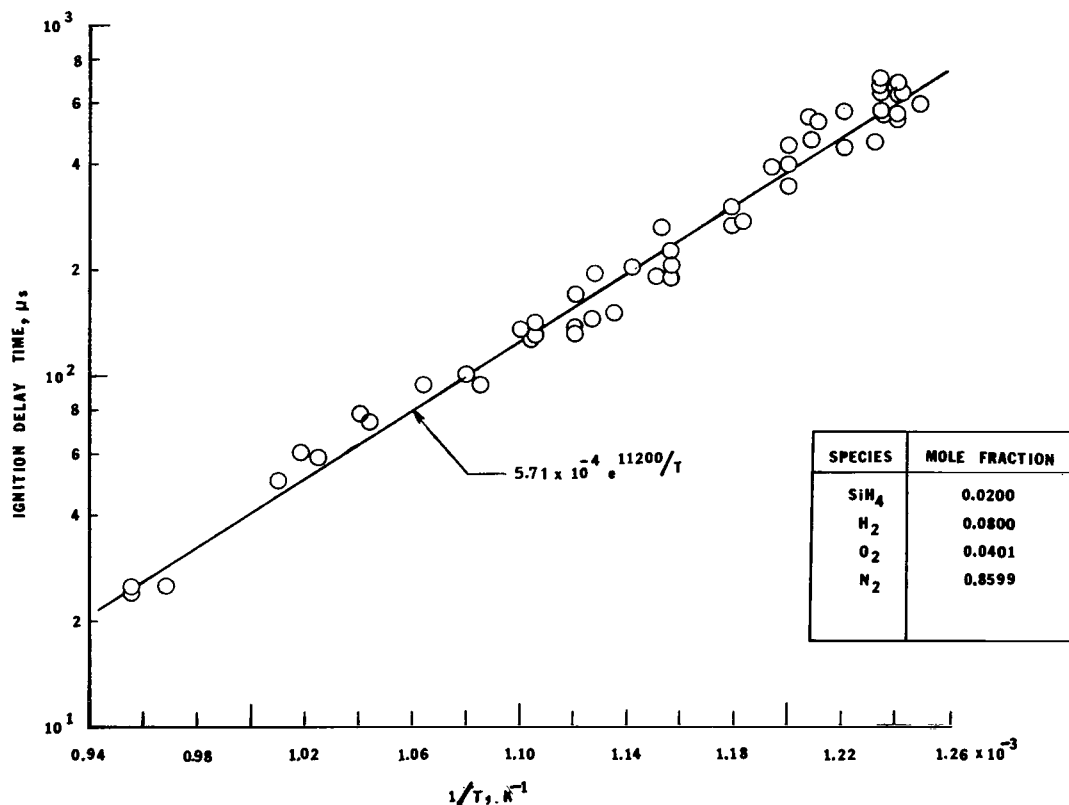


Figure 3.- Variation of ignition delay time with reciprocal temperature for mixture I. Silane-oxygen equivalence ratio of 1.0; Pressure = 1.25 atm.

of 1.0 and a pressure of 1.25 atm. The variation of the ignition delay times with temperature for a silane-oxygen equivalence ratio of 0.5 and a pressure level of 1.35 atm is shown in figure 4. To further substantiate that silane enhances

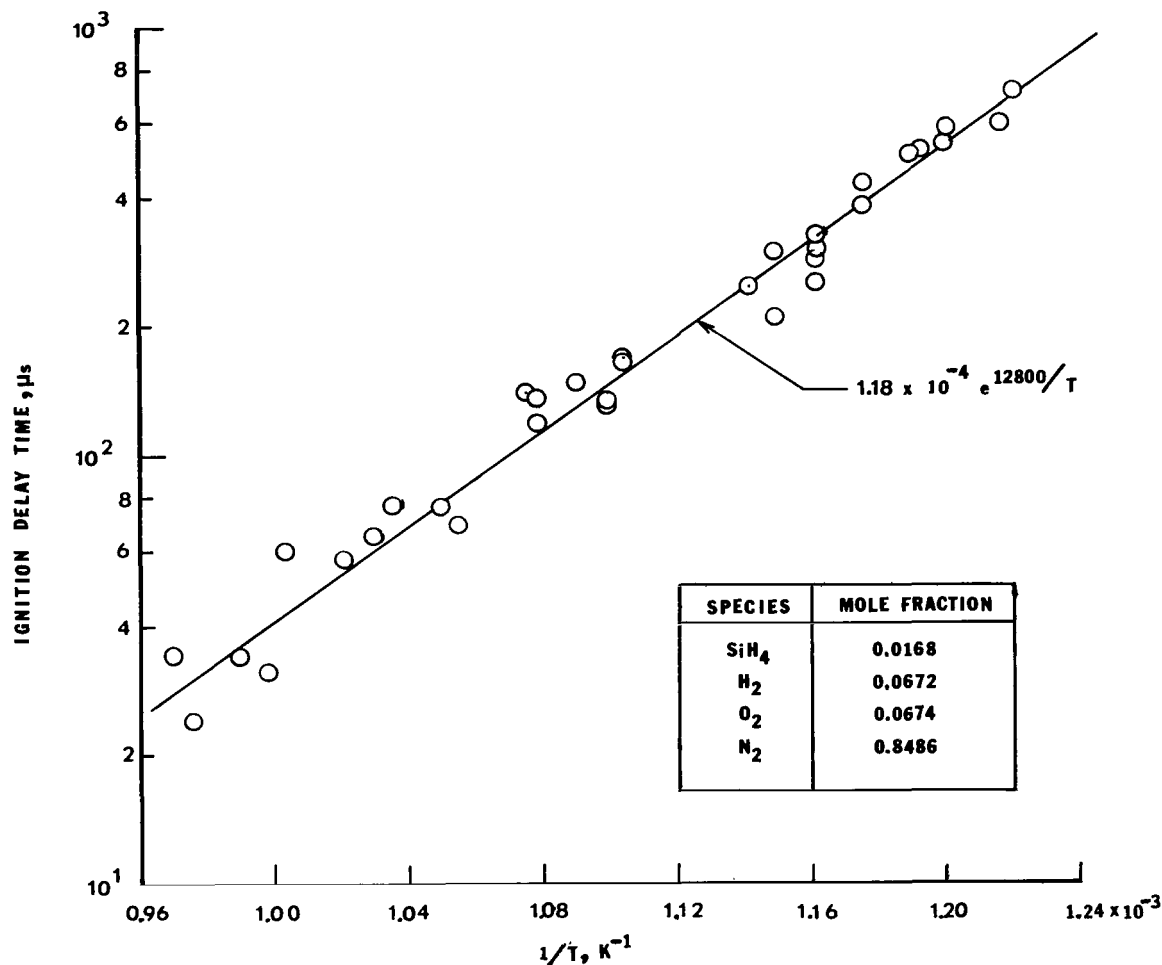


Figure 4.- Variation of ignition delay time with reciprocal temperature for mixture II. Silane-oxygen equivalence ratio of 0.5; Pressure = 1.35 atm.

ignition, experiments with similar mixtures that did not contain silane were conducted over the same pressure and temperature range used with the silane-hydrogen mixtures. Ignition did not occur during the available test times ($\approx 1000 \mu\text{s}$). The lines in figures 3 and 4 represent least-squares curve fits to the data presented in tables II(a) and II(b). The curve fit shown in figure 3 resulted in the equation

$$\tau = 5.71 \times 10^{-4} e^{11200/T}$$

to describe the ignition delay time τ (in microseconds) as a function of reflected shock temperature T (kelvin) for the mixture with a silane-oxygen equivalence ratio

of 1.0 and a test pressure of 1.25 atm. The least-squares curve fit of the data shown in figure 4, obtained with a silane-oxygen equivalence ratio of 0.5 and a test pressure of 1.35 atm, yielded the equation

$$\tau = 1.18 \times 10^{-4} e^{12800/T}$$

COMPARISON BETWEEN EXPERIMENTAL RESULTS AND KINETIC MODEL

Beach et al. (ref. 2) proposed a mechanism for the combustion of silane which was assembled by analogy with the methane oxidation mechanism. The reactions and rate coefficients which made up the mechanism are listed in table III. Most of the rate coefficients for the silane reactions were estimated, and several were adjusted to fit the experimental results of Strater (ref. 7), who studied the combustion of silane in a flow reactor over the temperature range from 500 K to 700 K.

Thermochemical properties were unavailable for some of the chemical species needed to develop a silane analog to a methane reaction mechanism. It was necessary, therefore, to estimate thermochemical property data for those species not in JANAF (ref. 4) or the open literature. As an example, the thermochemical data for the compounds SiH_2 and SiH_3 were estimated by analogy to the "families" of curves reported for hydrocarbons in reference 8. The assumption was made that silane is analogous to the methane family with species CH , CH_2 , CH_3 , and CH_4 , and the family of SiH , SiH_2 , SiH_3 , and SiH_4 was generated. The data for SiH_2 and SiH_3 were estimated to fit between the JANAF (ref. 4) data for SiH and SiH_4 , in a manner similar to that of reference 8. Other compounds, such as SiH_2O and HSiO , were assumed to be present in the silane mechanism by analogy with methane. Thermochemical data for these compounds were estimated also. The analytical computer program described in reference 9 was used to calculate the temperature and pressure history after passage of a reflected shock wave. To simulate the conditions after passage of a reflected shock wave, the computer program was operated in a constant volume (density) manner as described in reference 6.

A comparison of the ignition delay measurements with the calculated ignition delay times for mixture I is shown in figure 5. Even though the mechanism predicts significant ignition enhancement over that for no silane (ref. 2), the measured enhancement is greater than predicted by the model. Considering the uncertainties in the silane kinetic mechanism and the fact that it was assembled and optimized by comparison with experimental results from a low temperature (500 K to 700 K) study of silane oxidation (ref. 7), the difference of a factor of 5 between the calculated and experimental results is reasonably good. However, the fact that a difference exists points out the need for further refinement of the reaction mechanism. In addition, better estimates of the thermochemical properties of the silicon-containing intermediates are needed to increase the reliability of the model.

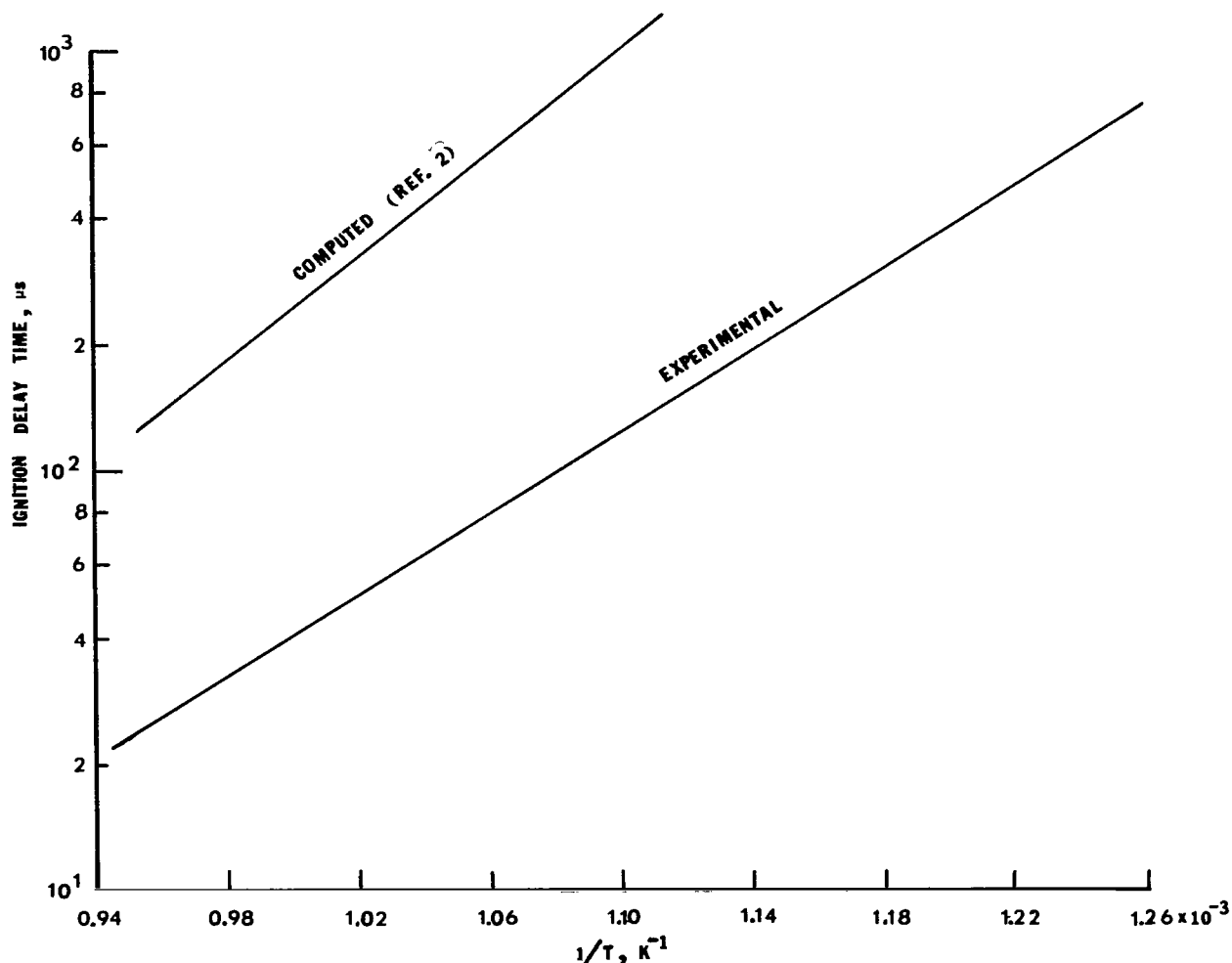


Figure 5.- Comparison of theoretically calculated ignition delay times with experimentally measured data for mixture I.

CONCLUDING REMARKS

Ignition delay times for mixture I (2.00 percent silane, 8.00 percent hydrogen, 4.01 percent oxygen, and 85.99 percent nitrogen) and mixture II (1.68 percent silane, 6.72 percent hydrogen, 6.74 percent oxygen, and 84.86 percent nitrogen) have been determined in a chemical kinetic shock tube with heating generated behind the reflected shock wave. The ignition delay times were measured at initial temperatures between approximately 800 K and 1050 K at pressures of 1.25 and 1.35 atm. The mixtures represented silane-oxygen equivalence ratios of 1.0 and 0.5, respectively. Tests conducted with mixtures containing no silane failed to ignite over the same temperature-pressure regime. This definitely indicated enhancement of ignition through the use of silane. The mixtures containing silane required from 24 to 752 μs to ignite after passage of the reflected shock wave. The measured ignition delay times were plotted against reciprocal temperature and curve-fitted by the least-



squares regression method. The equation for ignition delay time τ (in microseconds) as a function of postshock temperature T (kelvin) for the silane-oxygen equivalence ratio of 1.0 was

$$\tau = 5.71 \times 10^{-4} e^{11200/T}$$

For a silane-oxygen equivalence ratio of 0.5, the equation was

$$\tau = 1.18 \times 10^{-4} e^{12800/T}$$

Thermochemical properties and chemical kinetic coefficients were estimated and used in a computer model of the chemical system behind a reflected shock wave. The chemical kinetic package and estimated thermochemical properties, based on analogy to the methane system, yielded a comparison which was closer than expected to the experimentally observed values, especially considering that the estimated theoretical values were developed from a scarce amount of data. If the use of silane as a combustion initiator is to be investigated in greater detail, estimated thermochemical properties and reaction rate coefficients must be replaced with measured or calculated values from spectrometric data.

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December 3, 1982

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TABLE I.- COMPOSITION OF TEST GAS MIXTURES

(a) Mixture I (silane-oxygen equivalence ratio of 1.0)

Gas	Mole-percent
SiH ₄	2.00
H ₂	8.00
O ₂	4.01
N ₂	85.99

(b) Mixture II (silane-oxygen equivalence ratio of 0.5)

Gas	Mole-percent
SiH ₄	1.68
H ₂	6.72
O ₂	6.74
N ₂	84.86

TABLE II.- IGNITION DELAY TIMES

(a) Mixture I (silane-oxygen equivalence ratio of 1.0)

[Pressure = 1.25 atm]

Reflected shock temperature, T, K	Ignition delay time, τ , μ s	$1/T$, K^{-1}
807	635	1.239×10^{-3}
815	470	1.220
806	635	1.241
826	433	1.211
812	460	1.232
820	443	1.220
845	272	1.183
882	149	1.134
893	137	1.120
893	170	1.120
893	129	1.120
876	204	1.142
877	142	1.127
865	204	1.156
865	187	1.156
940	94	1.064
904	128	1.106
904	128	1.106
922	24	1.105
910	135	1.099
866	226	1.155
887	198	1.127
860	267	1.153
870	190	1.150
835	345	1.198
850	268	1.177
850	300	1.177
807	689	1.239
835	400	1.190
835	452	1.198
846	391	1.192
811	559	1.233
807	623	1.233
811	633	1.233
811	573	1.232
811	628	1.233
801	590	1.248
807	534	1.239
807	558	1.239
922	93	1.085
927	100	1.079
958	74	1.044
962	78	1.040
976	58	1.025
983	60	1.017
990	50	1.010
1046	25	.906
1033	25	.968
1046	24	.956

TABLE II.- Continued

(b) Mixture II (silane-oxygen equivalence ratio of 0.5)

[Pressure = 1.35 atm]

Reflected shock temperature, T, K	Ignition delay time, τ , μs	$1/T$, K^{-1}
930	140	1.075×10^{-3}
1032	34	.969
978	57	1.022
832	582	1.202
838	512	1.193
850	433	1.176
971	65	1.030
927	118	1.078
966	77	1.035
1011	34	.982
960	60	1.042
1025	24	.976
910	135	1.099
917	148	1.091
948	69	1.055
952	76	1.050
860	752	1.163
910	131	1.099
876	248	1.142
870	300	1.149
850	382	1.176
828	530	1.201
860	304	1.163
840	500	1.190
818	708	1.222
822	599	1.217
870	210	1.149
905	167	1.105
860	326	1.163
860	284	1.163
905	169	1.105
928	135	1.078
1002	31	.998

TABLE III.- SILANE-HYDROGEN REACTION MECHANISM

[From ref. 2]

Reaction	*A	*n	*E _R
[†] M + SiH ₄ → SiH ₃ + H + M	1.00 × 10 ¹⁸	0	68 051
SiH ₄ + H → SiH ₃ + H ₂	2.50 × 10 ¹⁵	0	3 700
SiH ₄ + O → SiH ₃ + OH	8.50 × 10 ¹³	0	3 850
SiH ₄ + OH → SiH ₃ + H ₂ O	5.70 × 10 ¹³	0	5 000
SiH ₃ + O ₂ → SiH ₂ O + OH	5.70 × 10 ¹³	0	7 000
SiH ₃ + O → HSiO + H ₂	1.00 × 10 ¹⁵	0	0
M + SiH ₂ O → HSiO + H + M	5.00 × 10 ¹²	.736	30 000
SiH ₂ O + H → HSiO + H ₂	2.00 × 10 ¹⁵	0	800
SiH ₂ O + O → HSiO + OH	2.00 × 10 ¹⁵	0	3 500
SiH ₂ O + OH → HSiO + H ₂ O	2.00 × 10 ¹⁵	0	0
M + HSiO → SiO + H + M	1.00 × 10 ¹⁵	0	23 000
HSiO + H → SiO + H ₂	1.00 × 10 ¹⁵	0	2 300
HSiO + O → SiO + OH	1.00 × 10 ¹⁵	0	2 400
HSiO + OH → SiO + H ₂ O	1.00 × 10 ¹⁵	0	1 400
SiO ₂ + OH → HSiO + O ₂	7.20 × 10 ¹⁰	.5	80 000
SiO + HO ₂ → HSiO + O ₂	7.70 × 10 ¹⁰	.5	4 900
SiO + OH → SiO ₂ + H	4.00 × 10 ¹⁵	0	4 300
SiO + O ₂ → SiO ₂ + O	1.00 × 10 ¹⁴	0	5 200

*The parameters A, n, and E_R refer to the rate coefficient equation $k = AT^n \exp(-E_R/RT)$. The rate coefficient units are s⁻¹ for unimolecular reactions, cm³/mole-s for bimolecular reactions, and cm⁶/mole²-s for termolecular reactions. The symbol E_R is the activation energy (cal/mole), R is the gas constant (1.987 cal/mole-K), and n is a temperature exponent factor obtained from empirical correlation.

[†]M is a third-body molecule.

TABLE III.- Concluded

[From ref. 2]

Reaction	*A	*n	*E _R
SiO + HO ₂ → SiO ₂ + OH	1.00 × 10 ¹⁴	0	2 000
SiO + O + [†] M → SiO ₂ + M	6.00 × 10 ¹⁶	0	0
H + O ₂ + M → HO ₂ + M	2.10 × 10 ¹⁸	-1	0
H ₂ + OH → H ₂ O + H	2.19 × 10 ¹³	0	5 150
H + O ₂ → OH + O	2.20 × 10 ¹⁴	0	16 800
O + H ₂ → OH + H	1.80 × 10 ¹⁰	1	8 900
H ₂ + HO ₂ → H ₂ O ₂ + H	3.00 × 10 ¹¹	0	18 680
M + H ₂ O ₂ → OH + OH + M	1.20 × 10 ¹⁷	0	43 500
H + HO ₂ → OH + OH	2.00 × 10 ¹⁴	0	1 800
H + OH + M → H ₂ O + M	8.40 × 10 ²¹	-2	0
O + O + M → O ₂ + M	1.38 × 10 ¹⁸	-1	340
O + H ₂ O → OH + OH	6.80 × 10 ¹³	0	18 360
H ₂ + O ₂ → OH + OH	1.00 × 10 ¹³	0	43 000
OH + HO ₂ → H ₂ O + O ₂	5.00 × 10 ¹³	0	1 000
O + HO ₂ → OH + O ₂	5.00 × 10 ¹³	0	1 000
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	2.00 × 10 ¹²	0	0
H + HO ₂ → H ₂ + O ₂	2.50 × 10 ¹³	0	700
H + H + M → H ₂ + M	6.40 × 10 ¹⁷	-1	0

*The parameters A, n, and E_R refer to the rate coefficient equation $k = AT^n \exp(-E_R/RT)$. The rate coefficient units are s⁻¹ for unimolecular reactions, cm³/mole-s for bimolecular reactions, and cm⁶/mole²-s for termolecular reactions. The symbol E_R is the activation energy (cal/mole), R is the gas constant (1.987 cal/mole-K), and n is a temperature exponent factor obtained from empirical correlation.

[†]M is a third-body molecule.

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